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POWDER DATA, UNIT CELL AND SPACE GROUP FOR FERROUS SULPHATE*

C. W. F. T. PISTORIUS

INSTITUTE OF GEOPHYSICS, UNIVERSITY OF CALIFORNIA,

LOS ANGELES 24 CALIFORNIA, U.S.A.

(*Received for publication, July 6, 1959*)

ABSTRACT. Anhydrous ferrous sulfate crystallizes in the orthorhombic system. The dimensions of the unit cell are $a_0 = 5.261$Å, $b_0 = 8.013$Å, $c_0 = 6.454$Å. The most probable space group is D^{17}_{2h}-Cmcm. The unit cell contains $(FeSO_4)_4$.

INTRODUCTION

Among compounds of the general formula MRO_4 there are some whose crystal properties, in spite of their simple composition, are still unknown. Such compounds are, for example, the anhydrous sulphates of the bivalent metals copper, iron, manganese and cobalt.

Our present inadequate knowledge of the crystallographic properties of these compounds is mostly due to the fact that they either form unstable, very hygroscopic crystals which are difficult to handle for x-ray analysis, or else do not form single crystals of satisfactory dimensions, but only a fine microcrystalline powder. $FeSO_4$ is one of the latter.

Recently, however, Dimaras (1957) succeeded in growing single crystals of $NiSO_4$ which possessed a sufficient size to enable him to determine the unit cell and space group. The present investigation was undertaken in the expectation that $FeSO_4$ would be isostructural with $NiSO_4$, and that an unambiguous assignment of the powder pattern of $FeSO_4$ could be made in analogy to the known pattern of $NiSO_4$.

EXPERIMENTAL

Fresh reagent grade $FeSO_4 \cdot 7H_2O$ was obtained from Merck. The company's analysis of the purity of the compound was as follows: Insoluble substances 0.010%, chloride (as Cl) 0.001%, phosphate (as PO_4) 0.003%, alkalies and earths 0.05%, copper (as Cu) 0.005%, ferric iron (as Fe) 0.010% and zinc (as Zn) 0.005%.

A weighed quantity of $FeSO_4 \cdot 7H_2O$ was heated to 150°C in vacuum for a period of three hours to drive off $6H_2O$. The product was then heated to 350°C

* Publication no. 155 of the Institute of Geophysics.

in a nitrogen atmosphere for one hour (Hedvall and Heuberger 1923). The weight loss agreed with the expected value.

The x-ray powder diffraction pattern of the resulting $FeSO_4$, ground into a paste with petroleum jelly, was obtained at 26°C in a Norelco high angle recording diffractometer, using FeK_α radiation ($\lambda = 1.9373$Å) and a Mn filter. The scanning speed was $1/8°(2\theta)$ per minute High-purity sodium chloride was used an as internal standard.

TABLE I

Spacings of anhydrous ferrous sulphate

observed *d*-spacing in Å	calculated *d*-spacing in Å	hkl	relative intensity in Å
4.373	4.398	110	27
3.982	4.006	020	16
3.045	3 634	111	84
3 408	3 404	021	36
2 618	2.631, 2.602	200, 112	100
2 371	2.382	130	29
2.051	2 039	202	17
1 993	2.003	040	10
1 919	1 913, 1.916	041, 132	7
1.825	1.817	222	23
1 706	1.702	042	30
1.609	1.613	004	6
1.589	1 594, 1 596	240, 133	5
1 546	1.547	241	5
1.520	1 515, 1.513	114, 312	10
1.462	1.466, 1 466	043, 330	8
1.431	1 429	242	30
1.385	1 385	152	5
1.314	1.315	400	5
1.284	1.281	243	4
1.251	1.250	420	4
1.094	1 099	440	7

RESULTS

The powder pattern obtained was almost exactly identical to that of $NiSO_4$, of which the powder pattern is listed in the ASTM powder data card file. However, it was totally different from the unassigned ASTM card for $FeSO_4$. Presumably the former measurements were made on oxidized or incompletely hydrated material.

All the observed diffraction peaks—which were rather broad, due to poor crystallization—could be satisfactorily assigned as due to an orthorhombic lattice with the following unit-cell dimensions, as obtained from a least-squares treatment :

$$a_0 = 5.261 \pm .010 \text{Å}.$$
$$b_0 = 8.013 \pm .005 \text{Å},$$
$$c_0 = 6.454 \pm .005 \text{Å}.$$

The axial ratios are

$$a_0 : b_0 : c_0 = 0.6566 : 1 : 0.8054.$$

The calculated density of $FeSO_4$ at 26°C, assuming 4 molecules per unit cell, is 3.707 gm/cm^3. The experimental value is 3.346 gm/cm^3 (Thorpe and Watts 1880). It is probable that, as Dimaras (1957) found in the case of $NiSO_4$, the crystallites have an incomplete internal development due to cavities, consequently causing a spuriously low macroscopic density.

The observed and calculated d-spacings, assigned indices and observed relative intensities are listed in Table I. The pattern is completely analogous to that of $NiSO_4$, and it consequently seems safe to assume that the space group is also the same, viz. D^{17}_{2h}—Cmcm.

As the unit cell contains four molecules $FeSO_4$, it is necessary to arrange in it four Fe, four S and sixteen O atoms. The space-group symmetry Cmcm possesses three four-fold positions. Two of these, position (a) (0, 0, 0; 0, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and position (b) (0, $\frac{1}{2}$, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, 0; $\frac{1}{2}$, 0, $\frac{1}{2}$) coincide with symmetry centers, while the third position (c) ($0, y, \frac{1}{4}$; $0, \bar{y}, \frac{3}{4}$; $\frac{1}{2}, \frac{1}{2}+y, \frac{1}{4}$; $\frac{1}{2}, \frac{1}{2}-y, \frac{3}{4}$), with one degree of freedom, lies on a two-fold axis. Because of the presumed tetrahedral arrangement of the O atoms around the S atoms, the only possible positions of the S atoms are (c). The SO_4 tetrahedron is further oriented by the symmetry in such a way that its two-fold axis coincides with the $(0, y, \frac{1}{4})$ axis.

In this way the O atoms occupy eight-fold positions, and, in particular, the O atoms of one pair lie on the $(0, y, z)$ plane while those of the other pair lie on the $(x, y, \frac{1}{4})$ plane. The Fe atoms must necessarily occupy one of the four-fold positions (a) or (b).

ACKNOWLEDGMENTS

The author wishes to thank Mr. Edwin Sharp for his assistance, and Mr. Lawrence Knight for technical aid in connection with the X-ray equipment.

REFERENCES

Dimmus, P. L., 1957, *Acta cryst.*, **10**, 313.
Hedvall, J. A. and Heuberger, J., 1923, *Z. anorg. Chem.*, **128**, 2.
Thorpe, T. E. and Watts, J. L., 1880, *J. Chem. soc.*, **37**, 116.